



## Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact [support@jstor.org](mailto:support@jstor.org).

## II.

## RE-EXAMINATION OF SOME OF THE HALOID COMPOUNDS OF ANTIMONY.

BY JOSIAH P. COOKE, JR.,

*Erving Professor of Chemistry and Mineralogy in Harvard College.*

OUR chief object in this paper is to describe some remarkable crystallographic and chemical relations of antimonious iodide, first noticed during the investigation of which an account has just been given; but we will also take the opportunity to give the results of some observations upon antimonious chloride and antimonious bromide, as well as upon the oxichlorides, oxibromides, and oxi-iodides of antimony, all of which have more or less bearing on the principal subject.

ANTIMONIOUS CHLORIDE ( $\text{SbCl}_3$ ).

Very perfect and brilliant crystals of antimonious chloride can be made in one of two ways, and both methods yield crystals of the same general form and habit.

The first method consists in cooling a saturated solution of the chloride in carbonic disulphide. Antimonious chloride is very soluble in this liquid, when near its boiling point; but the solubility diminishes very rapidly with a falling temperature, and, when the solution is cooled with a freezing mixture, by far the larger part of the substance crystallizes out. During our experiments, we frequently noticed, with these solutions of antimonious chloride, the phenomena of supersaturation. A solution saturated at the boiling point of the solvent, and cooled in a clean glass flask, may, if undisturbed, remain liquid for an indefinite time; but, the moment a bit of the solid substance is dropped in, the crystals form with great rapidity, and the very marked rise of temperature which we have observed under these circumstances indicates that the crystallization is attended with the liberation of an unusually large amount of latent heat. Similar phenomena of supersaturation we noticed with solutions of antimonious bromide, which, although less soluble than the chloride, dissolves very freely in the same solvent;

but, with the solutions of the far less soluble antimonious iodide (in disulphide of carbon) the phenomena were not perceptible. It is evident, from these facts, that the phenomena of supersaturation are not confined to aqueous solutions, or to substances which take into their crystalline structure a portion of the solvent, like water of crystallization.

The second method of obtaining crystals of antimonious chloride, is the familiar process of pouring off the still fluid portion, after the melted substance has partially solidified. Since, in consequence of the low temperature at which it hardens and the large amount of latent heat evolved in the process, the chloride *sets* comparatively slowly, the crystals form under these circumstances with great perfection, and are left clear and brilliant when the fluid is poured off.

It is very easy to obtain, by either of these methods, very perfect crystals, with very brilliant faces; but to measure these crystals is a difficult problem, which we have as yet been able to solve only imperfectly. Antimonious chloride is so very hygroscopic, that, during the short time required to isolate the crystals and mount them in tightly corked glass-tubes (and under such protection the measurements were made), the faces so far lost their lustre as to render the reflected image of the goniometer signal indefinite. Hence, the results given below are to be regarded as only approximate, and may be in error to the extent of even a degree. The angles of the vertical prism are probably the most accurate, because the crystals could be most quickly mounted with this dome parallel to the axis of the tube. The two domes present were measured on different crystals, and the angles given are the results of what were considered the most favorable observations. When the crystal was once mounted, its position could not be shifted; for the antimonious chloride attacked the wax used, and this circumstance added to the difficulties attending the necessary manipulations in measurements with the goniometer.

The crystals of antimonious chloride are trimetric, and have the same general habit whether obtained by the one or the other of the two methods just described. The chief difference is a greater or less degree of elongation in the direction selected as the vertical axis, — a difference which is shown by Figs. 1 and 2 of Plate I. The crystals were examined with a polarizing microscope arranged as a stauroscope; and we observed that, when the crystals were resting on either of their planes, so that the light passed between two opposite and parallel surfaces, the principal optical sections were, as nearly as could be observed, either parallel or normal to the prismatic edges. This, although not

conclusive evidence in itself, confirms the conclusion in regard to the crystalline system, which was based on the symmetry of the external form.

### CRYSTALLINE FORM OF ANTIMONIOUS CHLORIDE.

#### ORTHORHOMBIC SYSTEM.

Forms {110} and {011}

Figs. 1 and 2, Plate I.

$$a = 1.263 \quad b = 1 \quad c = 1.109$$

Angles between normals.

$$110 \text{ on } 1\bar{1}0 = 103^\circ 16'$$

$$011 \text{ „ } 0\bar{1}1 = 115^\circ 57'$$

In order to obtain the specific gravity of antimonious chloride in the solid state, we filled a specific-gravity bottle nearly full of the melted substance; and, after the mass had “set,” we added (so as to completely fill the bottle) some rock oil, which had been rectified over sodium. We then kept the bottle in the exhausted receiver of an air-pump, long enough to remove any entangled air; and, finally, after inserting the ground stopper and wiping away the excess of oil, we took the weight at a carefully regulated temperature. We could find no liquid on which antimonious chloride does not act, to a greater or less extent. It acted slightly even on this rectified rock oil, although only very slowly; so that, by working as quickly as possible, we must have obtained a result which was at least nearly accurate. We used the same preparation of antimonious chloride, of which a complete analysis is given on page 70 of the previous paper. The weight taken was 19.9575 grammes, which displaced 5.0212 grammes of oil. The specific gravity of the rock oil at  $26^\circ$ , referred to water at the same temperature, was 0.7693; and we found —

$$\left. \begin{array}{l} \text{Specific gravity of Antimonious Chloride at } 26^\circ, \\ \text{referred to rock oil at same temperature . . .} \end{array} \right\} 3.976$$

$$\left. \begin{array}{l} \text{Specific gravity of Antimonious Chloride at } 26^\circ, \\ \text{referred to water at same temperature . . .} \end{array} \right\} 3.064$$

The melting point of antimonious chloride was determined by observing the constant temperature during the slow crystallizing of a considerable mass of the melted substance, the liquid being stirred

meanwhile with the bulb of the thermometer, which was immersed up to the division on the stem marking  $15^{\circ}$ . The preparation used in this determination was that designated by *f*, in the table on page 40; and we obtained, as the

Melting point of Antimonious Chloride,  $72^{\circ}$  C.

We obtained also, and in the usual way, for the

Boiling point of Antimonious Chloride,  $216^{\circ}$  C.

In several instances, while rectifying this substance as described in the last paper, we followed the boiling point, and observed that it was constant, during the whole period of the distillation.

#### ANTIMONIOUS BROMIDE ( $\text{SbBr}_3$ ).

The methods used for preparing and purifying the bromide, as well as the chloride, of antimony, have been so fully described in the previous paper that no further details are necessary here. We obtained very brilliant crystals of the bromide, not only by the two methods described under the last head, but also by sublimation with the apparatus represented on page 57 of this volume. As treated in either of these ways, the habit of the substance is to form needle-shaped crystals, which run out into fine points without definite terminations, and often group themselves into irregular bundles, — a very common feature of this type of crystals. Only on one occasion (then by slowly cooling a solution in disulphide of carbon) did we obtain well terminated crystals; and, although we afterwards tried again and again, we have not yet been able to reproduce them. Unfortunately, moreover, before we were ready to make our measurements, the small terminal planes of these crystals had already become tarnished by the atmosphere. For, although the substance is so much less hygroscopic than antimonious chloride, yet the crystals of antimonious bromide soon lose their sharpness, if exposed even to what we call our dry winter air. Hence, we were not able to measure the angles between the terminal planes with a reflective goniometer. The approximate value of 101 on 100, we obtained by measuring the corresponding edge angle under the microscope, and by frequent repetitions of the measurement on different crystals, or on the two sides of the same crystal, securing as great accuracy as is possible under such circumstances; but the result cannot be relied upon within one or two degrees.

## CRYSTALLINE FORM OF ANTIMONIOUS BROMIDE.

## ORTHORHOMBIC SYSTEM.

Forms {100}, {010}, {101}, {110}, {111 (?)}

Fig. 3, Plate I.

$$a = 1.224 \quad b = 1 \quad c = 1.064.$$

Angles between normals.

$$010 \text{ on } 110 \qquad 39^\circ 14'$$

Also, measured with microscope.

$$101 \text{ on } 100 \qquad 49^\circ \text{ approximately}$$

Calculated.

$$101 \text{ ,, } 101 \qquad 82^\circ$$

$$111 \text{ ,, } 111 \qquad 72^\circ 4'$$

$$111 \text{ ,, } 010 \qquad 38^\circ 47'$$

$$111 \text{ ,, } 111 \qquad 61^\circ 30'$$

The octahedral angles were calculated on the assumption that the observed planes were those of a fundamental octahedron; but, although the intersections with 110 appeared to be parallel, yet the edges were too indefinite to give any certainty on this point.

We also examined the crystals of antimonious bromide with the polarizing microscope, and observed that one of the principal optical sections was parallel to the prismatic edge, whether the light passed normal to one or the other of the two pinacoids 010 and 100.\*

The specific gravity, in the solid state, of purified antimonious bromide was taken in precisely the same way as that of antimonious chloride:—

---

\* The only previous description of these crystals of which we have any knowledge was given by Nicklès, "Comptes Rendus," XLVIII. 837, in these words: "Le bromure d'antimoine se présente en octaèdres rhomboïdaux, parfois modifiés par des faces terminales; ils constituent alors des prismes aplatis de 69 degrés terminés par des pointements de 80 degrés; l'angle de deux faces contiguës de l'octaèdre est de 181 degrés (les minutes ont dû être négligées le cristal étant trop déliquescent)." In a later paper, "Journal de Pharmacie et de Chimie" (3), XLI. 142, a figure is given, and this description is essentially repeated, correcting the obvious misprint, 181 for 131; but, nevertheless, this error has been very generally copied. The crystals measured by Nicklès must have had a very different habit from any we have seen, and we have not been able to reconcile his description with our own observations.

Weight of Antimonious Bromide taken . . 32.2938 grammes.

Specific gravity referred to Kerosene at 23° . 5.386

„ „ Water at 23° . 4.148

By the same methods used with antimonious chloride, we made several determinations of both the melting and the boiling points of purified antimonious bromide, with the following results:—

Melting point of Antimonious Bromide 93° C.

Boiling point „ „ 280° C.

#### ANTIMONIOUS IODIDE ( $\text{SbI}_3$ ).

There are three crystalline conditions of antimonious iodide, — the hexagonal, the orthorhombic, and the clinorhombic or monoclinic, of which only the first has hitherto been described.

#### HEXAGONAL ANTIMONIOUS IODIDE.

Hexagonal crystals of iodide of antimony of a deep ruby red color can be readily obtained, either by cooling or by evaporating a saturated solution of this substance in disulphide of carbon, and this solution is easily prepared (as described in the previous paper) by shaking up, with finely pulverized metallic antimony until the color is discharged, a strong solution of iodine in the same solvent. These crystals were described by Nicklès, in connection with those of antimonious bromide, in the paper just referred to. He states that they are hexagonal, double pyramids, with a basal angle of 133°; and his description is referred to by Schneider,\* who also obtained hexagonal crystals, both from the disulphide of carbon solution, and also by subliming a mixture of antimonious sulphide with iodine. Schneider speaks of the crystals as brilliant, sharp, six-sided leaves or tables; but gives no additional measurements. All the crystals which we have examined (and we have seen the products of a great number of crystallizations) are combinations of a rhombohedron with its first obtuse rhombohedron and the basal planes, as shown in Figs. 4 and 5, Plate I. The habit of the crystals, however, differs very greatly with the conditions under which they are formed. When deposited during the rapid cooling of a solution saturated at the boiling point of the very volatile solvent, they are, as Schneider states, small and leaf-like, with a very definite hexagonal outline; but still, when seen with a microscope by

---

\* Poggendorff, *Annalen*, cix. 610, 1860.

reflected light, the rhombohedral planes can be distinguished on the edges. When formed during the slow evaporation of the solvent, they are, as Schneider also noticed, larger and more tabular. We ourselves have further observed, that, when the solution contains an excess of iodine, the rhombohedral planes become much more dominant, and the crystals greatly elongated in the direction of the vertical axis. The basal plane is then often reduced to a small triangular face; and we have seen crystals in which it had almost, if not wholly, disappeared. Among such crystals, we have observed macles hemitroped on the basal section; and the rhombohedral planes are frequently strongly striated parallel to the basal edges.

Under circumstances similar to those just mentioned, especially when the amount of free iodine in the solution is proportionally large, the crystals frequently group together into stars with six rays. These rays are formed by crystals elongated in the direction of one of the diagonals of the hexagonal section, and each by itself has the outward aspect of the trimetric system. The rays often branch, but in all cases at the constant angles of  $60^\circ$  or  $120^\circ$ ; and the whole group preserves a more or less regular hexagonal outline. Such groups may be regarded as skeleton crystals, and their formation is probably determined by a deficiency of the substance of the crystals in the mixed solution from which they are formed. The polariscope shows that they have throughout an hexagonal structure, and their formation indicates a tendency in the crystals of this substance (often manifested in single crystals to a less degree) to excessive development in a single direction, thus imitating a trimetric habit. As we shall hereafter see, this habit is not without its significance.

When iodide of antimony is sublimed as described in the previous paper (page 57), and also by Schneider (*loc. cit.*), it condenses in very broad thin leaves or plates, which hang from the surfaces of attachment by their edges. Even these, however, frequently exhibit on their free edges, not only the hexagonal outline, but also the rhombohedral planes; and the polariscope shows that the surfaces of the leaves are simply widely extended basal planes.

Iodide of antimony is not hygroscopic, and for this reason the crystals present conditions which are more favorable for accurate measurements than the crystals either of the chloride or of the bromide of the same element. Nevertheless, our results were not as constant as the brilliancy of the crystals led us to expect; and we met with variations in the angles which we could not ascribe solely to imperfections of the faces or to other causes of inexactness in the measurements. The



uncertainty thus arising does not, however, amount to more than a few minutes. We give the results obtained with the most perfect crystals we could find, on which we were able to measure all the angles of the principal dome between the two basal planes.

### CRYSTALLINE FORM OF ANTIMONIOUS IODIDE.

#### HEXAGONAL VARIETY.

Forms {111}, {100}, {011}

Figs. 4 and 5, Plate I.

Angles measured between normals.

111 on 100	72° 28'
100 „ 0II	49° 22'
0II „ III	58° 8'
	<hr/>
	179° 58'

These measurements correspond to the dimensions of a modified rhombohedron in which the axes of Miller's system make with each other the angle of  $54^{\circ} 40'$ , or the vertical axis of Naumann's system has the value  $C = 2.769$ . The crystals cleave readily parallel to the basal plane.

Angles between normals.	Calculated.	Measured.
111 on 100	72° 38'	72° 28'
111 „ 110	49° 23'	49° 22'
110 „ 00I	57° 59'	58° 8'
100 „ 010	111° 30'	
110 „ 011	94° 28'	
100 „ 110	55° 45'	

The crystals are optically uniaxial with very strong negative double refraction, and the broad plates obtained by sublimation furnish excellent objects for the polariscope; but such preparations are not durable if exposed to the atmosphere, for a reason which will appear further on. The rings of the interference figure, as seen by common light, are nearly black, but with strong-colored fringes, — red on the inside, and greenish yellow on the outside. This is a natural result of the selective absorption of this highly colored medium; but the effect is, nevertheless, very striking.

Evidently, then, so far as yet appears, the iodide of antimony is not isomorphous with the corresponding bromide and chloride, although there is no group of compounds which we should by analogy expect to find more closely isomorphous than the chloride, bromide, and iodide of the same element. It has been shown, however, by other crystallographers as well as by ourselves, that the hexagonal forms are closely related to the trimetric, and that when the angle of the rhombic prism becomes equal to or even closely approaches  $60^\circ$  or  $120^\circ$ , the last may imitate, if they do not actually assume, both the external aspect and internal structure of the first. We were, therefore, led to suspect that we had before us another example of such a relation, and that the iodide of antimony might thus be constructively isomorphous with its allied compounds. The following calculation, moreover, strongly sustained this view:—

The large development of the pinacoid planes (010 and 0 $\bar{1}$ 0) which is very characteristic of the crystals of bromide of antimony, besides the general form of these crystals (as shown by our figure), indicate very clearly that these pinacoids are the analogues of the basal planes of the hexagonal crystals of iodide of antimony; and, if so, then the isomorphism of the bromide and the chloride indicates that, for the last compound, the analogues of these planes would be a corresponding pair of pinacoids which does not appear on the actual crystals. Again, we find the analogue of the angle,  $120^\circ$ , on the hexagonal section of the crystals of antimonious iodide, in the angle  $98^\circ$ , between the planes 101 and  $\bar{1}$ 01 on the crystals of antimonious bromide; and although the corresponding planes do not appear on the crystals of antimonious chloride, yet the equivalent angle can be easily calculated, and will be found to be  $97^\circ 26'$ . If now we compare the tangents of the halves of these last two angles with  $\frac{2}{3}$  of the tangent of  $60^\circ$ , we shall obtain the following relations:—

$$\begin{array}{lll} \text{For SbCl}_3 & \text{tang. } 48^\circ 43' & = 1.139 \\ \text{,, SbBr}_3 & \text{tang. } 49^\circ & = 1.150 \\ \text{,, SbI}_3 & \frac{2}{3} \text{ tang. } 60^\circ & = 1.155 \end{array}$$

If, further, we take into consideration the third axis, this relation will appear still more close and simple. Making, then, in the crystals of antimonious chloride and bromide the half-axis  $c$  our unit, and regarding for the time, as the vertical axis, the half-axis  $b$ , which corresponds to the vertical axis of the hexagonal form, giving also to this last axis its known value,—we obtain the following comparison between

the axial dimensions of the two orthorhombic forms and of the hexagonal form, if referred to corresponding orthorhombic system of axes:—

$$\begin{array}{lll} \text{For SbCl}_3 & a = 1.139 & \overset{1}{b} = 0.902 \quad c = 1 \\ \text{,, SbBr}_3 & a = 1.150 & \overset{1}{b} = 0.940 \quad c = 1 \\ \text{,, SbI}_3 & a = 1.155 & \frac{1}{3} \overset{1}{b} = 0.923 \quad c = 1 \end{array}$$

It thus appears that, constructively, iodide of antimony is closely isomorphous with the two allied compounds, and the small apparent differences in the axial dimensions of the three forms are no greater than the uncertainties in these values themselves arising from the imperfect measurements of some of the angles.

But although the rhombic prism of  $60^\circ$  or  $120^\circ$  may imitate the external aspect of an hexagonal form, as is frequently the case with the micas and vermiculites, yet (as the optical relations of these very minerals show) the two classes of forms may still remain perfectly distinct; and it does not, therefore, by any means follow that the rhombic prism passes into the hexagonal system when the prismatic angle becomes  $120^\circ$ . We have, however, shown, in the paper just referred to, that, by a species of interlamination,—interlaminar macting, we may name it,—the orthorhombic crystals of foliated minerals frequently imitate the structure, as well as the forms, of the hexagonal system; and although there is an obvious distinction between such structures and homogeneous crystalline masses, like calcite or the substance we are considering, yet analogy would suggest, that, even the true hexagonal structure may result from a more fundamental macting of the same kind; and we advanced the theory, that it might be the result of what we called molecular macting. According to this theory, the *crystalline* molecules of hexagonal forms are, in some cases if not in all, groups of three simpler molecules, each of which (so far as its chemical constitution is concerned) is a unit in itself, and possibly under certain conditions may act as a unit in a crystalline structure, and probably always becomes isolated when the substance is converted into vapor. Our theory also assumes that the members of these groups are united among themselves in the same relative positions as the diagonals of a regular hexagon, so that the optically uniaxial character of hexagonal crystals is an effect of such grouping, and the hexagonal form an obvious result of the juxtaposition of the six-sided groups. Further, we suppose that the simpler molecules are of such a nature that, when united as individuals in positions parallel to each

other, they would form crystals having a rhombic section of  $60^\circ$  or  $120^\circ$ . The figures 1 and 2, which we reproduce from a previous paper, may help to give a more definite form to these conceptions; but

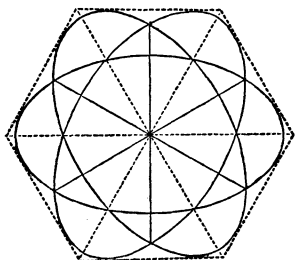


Fig. 1.

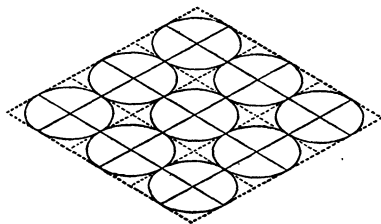


Fig. 2.

such representations are necessarily purely conventional symbols of conditions of which we have as yet no accurate knowledge, and to which, therefore, we can give no definite shape. The capability of such molecular macling as we have described may depend solely on the dimensions of the molecules; and in our figures we have represented such a condition, by giving to the sections of the molecules the form of ellipses of such dimensions that they can be inscribed in the rhomb of  $60^\circ$  and  $120^\circ$ . The conjugate diameters of this figure, when equal, subtend angles of  $60^\circ$  or  $120^\circ$ ; and if the poles of the molecules are, as would be natural, at the ends of these lines, then, when the molecules were grouped as shown in Fig. 1, the unlike poles would fall directly over each other; so that the attractive and repulsive forces, centring at the poles, would hold the parts firmly together. The same molecules, if placed parallel to each other (as in Fig. 2), would be also in a stable condition, and the resulting rhombic section would have angles of  $60^\circ$  and  $120^\circ$ . On the other hand, although ellipses of other dimensions might be united as in Fig. 2, so as to give rhombic sections of every possible angle, yet only with ellipses of the dimension we have described, or those closely approaching this condition, would such a grouping be stable as is represented by Fig. 1. Of course, the molecules must have three dimensions; and, as before intimated, the ellipses are only conventional modes of expressing conceptions which are necessarily very incomplete. These symbols, however, will give form to our theory, and show why, among a series of isomorphous compounds crystallizing in the rhombic system, we might expect to find hexagonal crystals wherever among the various molecular

magnitudes the necessary dimensions were realized, although it is probable that there are other conditions which must also concur to produce this result.

Evidently, we have before us just such an isomorphous series as our theory anticipates, — a series of closely allied substances, in which the orthorhombic passes into the true hexagonal structure; and this furnishes us with an excellent opportunity for testing the theory we have advanced. If the crystalline molecules of the hexagonal iodide of antimony are really groups of three of the chemical molecules of this substance, then we might hope to find another condition of this substance in which the molecules were united, as in the crystals of the allied substances presenting rhombic forms with the angles of  $60^\circ$  or  $120^\circ$ ; and, if such could be discovered, it would be reasonable to expect differences in the physical properties of the two isomers corresponding to the differences of structure. We were therefore led to search for a rhombic modification of the iodide of antimony, and with what success will soon appear. Before pursuing this subject, however, it will be best to describe some of the other physical properties of the hexagonal iodide.

The color of the hexagonal iodide of antimony is a brilliant vermilion red, which, however, in some preparations, is more or less tinged with yellow, in consequence of oxidation, and the formation of an oxiodide on the surfaces of the crystals. The solution of the iodide of antimony in sulphide of carbon has a greenish yellow color, resembling that of uranium glass, and strikingly contrasting with the brilliant red color of the crystals which have been formed from it, — a fact whose significance will hereafter appear.

We made five determinations of the specific gravity of the hexagonal crystals of iodide of antimony; using for the purpose different preparations, and taking the specific gravity under petroleum which had been rectified over sodium, — the only liquid we could find that did not act on the substance. Even the rectified petroleum, however, acted slowly on this, as it did on the allied substances; but, during the time occupied in the determination, the effect was very slight, and no considerable error could have been thus caused. The following are the results of these determinations, all made at a temperature of about  $24^\circ\text{C}.$ :—

No.	Weight taken in grammes.	Sp. Gr. at 24°, referred to water at same temp.
1.	6.9730	4.807
2.	10.1393	4.895
3.	5.3506	4.812
4.	7.8868	4.893
5.	2.1517	4.833
Mean value		4.848

We made four observations of the melting point of the hexagonal iodide. For the first, we used a large amount of material, and, by dipping the bulb of the thermometer in the melted mass, observed the constant temperature while it was slowly solidifying. In the other experiments, we melted a few crystals in a glass tube, heated by a bath of sulphuric acid in the usual way. The result in the first determination was  $167\frac{1}{2}^{\circ}$ ; in the last three, uniformly  $167^{\circ}$ , which is doubtless the true value. In the experiments with the tube, it was noticed that the point of solidification was about five degrees below the melting point.

Bringing together now the several results, we have the following comparison of the melting points of the three haloid compounds we have studied —

	Melting Point.	Differences.
Rhombic Antimonious Chloride	$72^{\circ}$	
		$21^{\circ}$
Rhombic Antimonious Bromide	$93^{\circ}$	
		$74^{\circ}$
Hexagonal Antimonious Iodide	$167^{\circ}$	

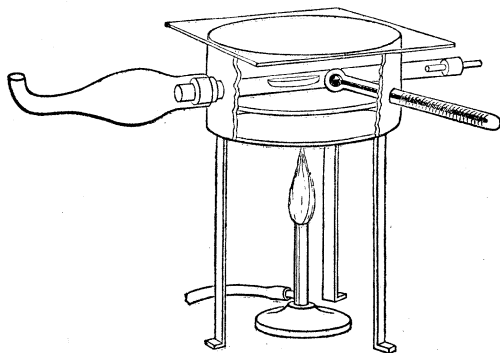
From this it appears, that, instead of the equal differences we should naturally expect, the difference between the last two values is between three and four times as great as the difference between the first two. According to all analogies, the melting point of the normal iodide of antimony should be  $114^{\circ}$ ; and the greatly higher value which we obtained is still another indication that the hexagonal iodide on which we experimented has an essentially different structure from that of the chloride or bromide of the same element with which it is here compared.

As yet, we have not been able to determine the boiling point of iodide of antimony with any accuracy. It is above, but apparently

only just above, the boiling point of mercury ; and, before the observation can be taken, it will be necessary to adapt some form of air thermometer to the necessary conditions.

#### ORTHORHOMBIC ANTIMONIOUS IODIDE.

We first met with this new substance while examining with a microscope the product obtained by subliming hexagonal iodide of antimony, in the apparatus represented in the accompanying figure, which we described in our previous paper (page 57) ; and we at once recognized,



both by its color and its form, the isomeric modification of which we were in search. It appeared in small greenish yellow sprays, sparingly distributed among the red plates of the hexagonal iodide. Its color was precisely that of the solution of the iodide in carbonic disulphide ; and, as shown in Plate II., the serrated edges of the crystalline sprigs presented very much the appearance of a picket fence, repeating at each point the characteristic angle of  $60^\circ$ .

It soon appeared that the yellow iodide was always formed when iodide of antimony was sublimed at a low temperature, and that this was the one condition necessary. Iodide of antimony begins to volatilize far below its melting point, even at  $100^\circ \text{C.}$  ; and, if it is sublimed between two watch-glasses at a temperature not exceeding  $114^\circ$ , the yellow modification is the sole product. It condenses them in beautiful feather-like sprays, on which, however, no definite form can be distinguished. The process, also, is exceedingly slow, and the product very small. A much larger yield is obtained when the iodide is sublimed at a temperature just above its melting point, in a current of inert gas sufficiently strong to sweep the vapor at once into a cool condenser, — conditions, which are perfectly realized in the apparatus we have described.

The yellow iodide generally forms but a small portion of the product of the sublimation; but, by carefully regulating the temperature and gas current, the proportion can be largely increased, and it can then be picked out among the scales of red iodide with which alone it is mixed. To obtain, however, in this way, a sufficient quantity of the yellow iodide for analyses wholly free from its more abundant red associate, would have been a very tedious task; but this was not necessary, in order to establish the perfect isomerism of the two substances. Of the material used in the following analyses, more than nine-tenths consisted of the yellow iodide of antimony; and as the results agree so closely both with theory and with the parallel analyses of the associated red iodide, which could be easily and perfectly isolated, there can be no question whatever that the two have the same percentage composition. These analyses are reproduced from our previous paper, in order to bring together all the facts bearing on the present discussion.

#### COMPARATIVE ANALYSES OF RED AND YELLOW IODIDE OF ANTIMONY.

RED HEXAGONAL.			YELLOW ORTHORHOMBIC.		
No.	Weight taken.	% of Iodine.	No.	Weight taken.	% of Iodine.
1.	1.1877	76.110	1.	0.4610	76.161
2.	2.3201	76.040	2.	0.3496	76.161
Mean value		76.075			76.161
Theory for $\text{SbI}_3$ , when $\text{Sb} = 120$ and $\text{I} = 127$					76.047

As additional evidence of the isomerism of these remarkable substances, we may here, in anticipation of a fuller discussion of the subject, mention a fact which would be by itself conclusive. At a very moderate elevation of temperature, the yellow iodide of antimony is completely converted into the red modification, and under such conditions that there can be neither loss nor gain of material in the process.

In measuring the angles of the rhombic plates as they lay in a normal position under the microscope, we found that we could obtain the sharpest results by projecting the image on a sheet of paper by means of a camera lucida. We were then able to adjust a straight edge to one after the other of two edges of the crystal, and draw the corresponding lines, whose angular divergence we then measured with a protractor. These measurements gave, for the acute angle of the



rhomb, as a constant result,  $60^\circ$ . The supplementary angles,  $120^\circ$ , are usually truncated; but not unfrequently (as shown on Plate III., Fig. 2) we meet with perfect terminations of this kind. When these occur on the same sprays as the acute angles, they uniformly appear in their proper relative positions, at right angles to the supplementary terminations, and we have frequently seen both terminations on the same rhombic plate. Less frequently, we find the sixty-degree angles truncated; and, as the result of such truncation, we have observed isolated hexagonal plates as perfect as those of the hexagonal iodide, from which outwardly they only differed in their color.

We have represented in Plate III., Fig. 1, a spray, presenting, for the most part, quite a different set of terminations from those before figured, which, although they are not quite so well defined as the others, nevertheless measure very constantly  $82^\circ$  and  $98^\circ$ . When found on the same sprays, the  $98^\circ$  terminations are, in general, parallel to the  $60^\circ$ , and the  $82^\circ$  to the  $120^\circ$ . Moreover, the  $98^\circ$  terminations are very frequently found bevelling the constantly recurring terminations of  $60^\circ$ , and, on the other hand, as often, the terminations of  $120^\circ$  bevel those of  $82^\circ$ .

Sometimes one of the two bevelling planes disappears, or, at least, is reduced to such small dimensions as to be imperceptible on the section as shown under the microscope. This kind of hemihedrism is shown, in the largest termination, both on Plates II. and III.

The angles  $98^\circ$  and  $82^\circ$ , or more accurately  $98^\circ 12' 50''$  and  $81^\circ 47' 10''$ , are the angles of the rhombic prism  $\{120\}$ , derived from the prism  $\{110\}$  of  $120^\circ$  and  $60^\circ$ . The relation of these two prisms is shown by the figure below the drawing, on Plate II.; and it will be noticed that all the termination edges in the drawing are parallel to one or the other of the lines whose relative positions are thus defined. It is a very remarkable property of the prism of  $120^\circ$ , that the derived prisms  $\{120\}$  and  $\{230\}$  have identically the same angles; the only difference being that the relative positions of these angles ( $98^\circ 13'$  and  $81^\circ 47'$ ) are reversed. This is shown in the same figure as before, where the prism  $\{230\}$  is also represented, but by dotted lines. The property referred to depends on the circumstance, that one-half and two-thirds of the tangent of  $60^\circ$  ( $\frac{\sqrt{3}}{2}$  and  $\frac{2}{\sqrt{3}}$ ) are reciprocals, and must therefore be the tangent and cotangent of the same angle, which is  $40^\circ 53' 35''$ , or one-half of the prismatic angle  $81^\circ 47' 10''$  named above. The same values are also equal, respectively, to the sine and cosecant of  $60^\circ$ , or to the cosine and secant of  $30^\circ$ . Not only,

therefore, is the rhombic prism of  $81^{\circ} 47'$  in either of the positions we have described, crystallographically compatible with the prism of  $120^{\circ}$ ; but also the two diagonals of the first bear to each other precisely the same relation which the lateral axes of a direct hexagonal prism or rhombohedron bear to those of the corresponding inverse forms.

The prism  $81^{\circ} 47'$  evidently corresponds to the prism of approximately the same dimensions, on the crystals of antimonious bromide {101}, Fig. 3, Plate I.; and this new condition of antimonious iodide is therefore closely isomorphous with the only known state of antimonious bromide and antimonious chloride.

The rhombic plates of the yellow iodide are quite uniformly marked parallel to the edges and sides of the rhomb, showing an evident tendency to the formation of domes and octahedrons, — a phenomenon so familiar in skeleton crystals.

Although the habit and grouping of the new crystals, the dimensions of their angles, and their relations to known forms, furnish very satisfactory evidence of their orthorhombic character, yet, from the nature of the case, this evidence is not demonstrative, and we were therefore desirous of obtaining the more conclusive evidence which optical characters give. The crystals, however, obtained as we have described, are usually so excessively thin that we were obliged to search a long time before we could find single plates sufficiently thick to give a distinct interference image. We did, however, at last obtain several plates which enabled us to observe all the important features of this instructive phenomenon. The hyperbolas were well marked, and separated by about six divisions of the scale of Groth's polariscope, which corresponds to an apparent angle between the optical axes of about  $36^{\circ}$ , although, on account of the thinness of the plate and consequent indefiniteness of the boundaries of the images, it was impossible to measure the angle exactly. The acute bisectrix was perpendicular to the faces of the plate, at least as closely as could be observed; the dispersion of the axes was very marked; and the hyperbolas were bordered with green on the concave and red on the convex side. Hence,  $q > \sqrt{}$ . No differences could be seen in the coloration between the two ends or the two sides of the image. A very perfect isolated hexagonal plate enabled us to determine that the plane of the optical axes was parallel to the sides of the hexagon, as in most micas, and as represented in Fig. 4. This plate was not sufficiently

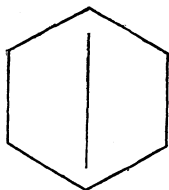


Fig. 4.

thick to show the hyperbolas distinctly; but, by combining it with a plate of a negative uniaxial crystal (tourmaline), we readily obtained the same familiar modification of the interference figure which is produced by a very thin plate of mica, and we were thus able, not only to determine that the character of the double refraction of our yellow plate was negative, but also to fix the position of the plane of the optical axes as just described.

We have stated that, at a very moderate temperature, the orthorhombic iodide changes to the hexagonal. It is now important to describe this remarkable phenomenon in detail. The change is not a gradual one; but suddenly, as soon as the required temperature is reached, a red spot appears, generally at one end of the rhombic plate, and then the red color rapidly spreads through the crystal, so that at any one point the change is instantaneous. Again, the change is attended with no disintegration of the crystal or loss of transparency; and not only the outline, but also all the minute markings, remain afterwards as sharp as before. Externally, there is simply a change of color from greenish yellow to bright red; and, by sudden cooling, it is perfectly easy to arrest the change so as to leave one part of the crystal red, while the rest remains yellow. The change, however, is attended with an entire alteration of structure; for the optically biaxial rhombic plate suddenly becomes absolutely uniaxial. Under the polarizing microscope, this change produces a very striking effect. In the dark field between crossed Nicols, the green rhombic plates show, of course, brilliant colors, whenever the diagonals of the rhomb lie obliquely to the planes of polarization; but, when the change takes place, a dark shadow suddenly spreads over each crystal, extinguishing this color, and then, on removing the analyzer, the very brilliant red color which the crystals have acquired appears. Under the polariscope, the sudden change from a biaxial to a perfectly uniaxial interference figure is still more striking. We have represented in Plate II. this remarkable phenomenon, as nearly as possible with a chromo-lithograph. The colors imitate very nearly, although not exactly, those of the natural crystals.

It becomes now a very interesting point to ascertain what is the exact temperature at which this singular change takes place. For this purpose, we heated on watch-glasses small quantities of the yellow crystals to different regulated temperatures, by means of a small air-bath; and in each experiment the temperature was maintained constant, at the selected point, for at least fifteen minutes. Thus we observed in one series of successive experiments: —

After heating to  $120^{\circ}$ , complete change.

” ” ”  $107^{\circ}$ , no change.

” ” ”  $110^{\circ}$  ” ”

” ” ”  $111^{\circ}$  ” ”

” ” ”  $112^{\circ}$  ” ”

” ” ”  $114^{\circ}$ , partial change.

” ” ”  $114^{\circ}$  complete ”

These results were completely confirmed by similar experiments, all of which indicated that  $114^{\circ}$  is very closely the temperature at which the change first begins; and this result is in complete accordance with the fact we have before stated, that the red iodide of antimony, when sublimed below  $114^{\circ}$ , is completely converted into the yellow modification.

It is evident, from the above experiments, that the point of the change we have been discussing is fully as sharply marked as the melting point of a solid; and, by referring to the table of melting points on page 84, it will be seen that  $114^{\circ}$  (the temperature at which the change takes place) is the very point at which, theoretically, the normal iodide of antimony ought to melt. Evidently, then, the yellow orthorhombic iodide does undergo incipient fusion at this point; and the molecules, becoming thus free to move, regroup themselves, and the more stable structure of the red hexagonal iodide results.

Here, then, we have certainly a most remarkable confirmation of the theory we have advanced in regard to the molecular structure of hexagonal forms. The two isomers we have just described have enabled us to show that absolutely the same external form is compatible with the differences of structure which distinguish the orthorhombic from the hexagonal system; and this fact, only probable before, is now demonstrated. Secondly, the conditions under which one of these isomers changes into the other indicates clearly that the difference between the two substances is simply a difference of grouping of the same molecules, and also that in the red modification the molecules are more intimately united than in the yellow. When we attempt to go further, and explain what this more intimate grouping is, we of course soon enter the region of theory; but the analogy furnished by the superimposed mica plates is certainly very strong. We may now be said to know that the structure of an hexagonal crystal can be produced by a more intimate grouping of the molecules of an orthorhombic crystal, whenever the dimensions are such that the same external form is compatible with these two types of internal structure. We also know that the

optical effect thus produced is like that obtained by superposing orthorhombic plates in a definite way. We further know, that, so long as these plates are kept of equal thickness, and their relative position maintained, the character of the effect is independent of their magnitude. Were the plates indefinitely thin and indefinitely small, there can be no question that a proportional effect would result, which, if indefinitely multiplied by passing the light through a great number of such superposed bundles, must give the same total effect as that obtained from a single bundle of thicker and larger plates. Now, molecules, in the sense in which we have used the term in connection with the theory we are discussing, are simply the elements of a certain definite orthorhombic structure, and have their analogues in small orthorhombic plates, — of mica, for example. By grouping these plates in a definite way, a certain optical effect is produced, without any change of external form. Precisely the same effect is the result of a change caused by heat in the mass of another orthorhombic material having the same crystalline form as the mica plates. Moreover, this change takes place at the exact temperature at which the parts of our protean material must acquire freedom of motion; and the obvious conclusion is, that in this change the elements of the orthorhombic crystal group themselves anew in the same way in which we group the mica plates in order to obtain a similar result. This is the outline of our argument. To enforce it, we have accessory facts, which show that the theory is in harmony with the accepted principles of polar forces and molecular mechanics, but these it is unnecessary to recapitulate. Of course, demonstration in such a case is out of the question; but we hope that we have been able to make clear that the theory of molecular macling, when stripped of the accessories which the conventional term "molecule" implies, is a close induction from the observed facts.

We have only one further point to make, before concluding the discussion of this portion of our subject. The color of the rhombic iodide of antimony is, as we have said, greenish yellow, recalling that of uranium glass; and, when either the yellow or the red iodide is dissolved in disulphide of carbon, the resulting solution has always the greenish yellow color of the first. In this solution, according to all theories, the molecules must be isolated; and the fact that this characteristic color is retained by the rhombic structure, and wholly changed in the hexagonal, is additional evidence that, while in the first the molecules act on the light as units, in the second their individual action must be modified by conditions depending on a peculiar mode of association.

## MONOCLINIC OR CLINORHOMBIC ANTIMONIOUS IODIDE.

We have stated in the previous article, that, when a solution of antimonious iodide in carbonic disulphide is exposed to the atmospheric air under the influence of the solar light, the compound in solution undergoes a gradual oxidation, iodine is set free, and oxi-iodide of antimony is precipitated. If, after this action has continued for twelve or fourteen hours in the direct sunlight, the very dark colored solution is distilled over a water bath (at a temperature which, even at the end of the process, should not exceed the boiling point of the solvent), the greater part of the free iodine passes over with the distillate; and, by repeating the distillation several times after adding more of the solvent to the residue in the retort, almost the whole of the free iodine can be removed. When now the residue is again dissolved in the same solvent, and the solution is allowed to evaporate spontaneously, there is generally deposited, at first, a crop of the crystals of the red hexagonal iodide; but, on decanting the remaining solution, we obtained, as a final result, a small amount of yellow monoclinic crystals similar to the one figured on Plate I. Fig. 6. These represent a third condition of antimonious iodide, which, being more soluble in disulphide of carbon, are very easily separated from the hexagonal iodide with which they are associated.

The yield of monoclinic crystals in the process we have described is uncertain and irregular; and as yet we have been unable to bring the conditions of their formation wholly under command. After much experimenting, however, we have reached a few definite conclusions. To the crystals prepared as above, there frequently adhered a perceptible amount of free iodine, and we naturally questioned whether this impurity might not have some influence on their production; but after repeatedly recrystallizing the hexagonal iodide from solutions containing even a large excess of free iodine, and obtaining none of the monoclinic modification, we concluded that the iodine had no further effect than to modify the habit of the hexagonal crystals as already described on page 78. In like manner, finding in certain cases, when crude disulphide of carbon was used, that the yield of monoclinic crystals was unusually large, we at once suspected that the impurities originally existing in the solvent might be the determining cause of the change of conditions in the crystals deposited from it. We therefore experimented with some very strong-smelling disulphide of carbon which had become yellow by long exposure to light and air; but we could not obtain the monoclinic crystals, except in uncertain

traces, until the disulphide with the dissolved iodide of antimony was exposed to the direct sun-rays for a long time, as above described. An equal amount of exposure before dissolving the iodide had no apparent effect. Again, after finding that iodide of antimony dissolved in disulphide of carbon is oxidized by ozonized air even in the dark, we sought to determine whether the monoclinic crystals were formed under these conditions independent of the action of the light; and, to this question also, our experiments returned a negative answer.

The production of the monoclinic crystals appears, therefore, to be independent of the oxidation of the iodide of antimony; although, like the latter, it is also due to the action of the sunlight. The effect seems to depend on a change produced in the solvent by the sun's rays, probably the same partial reduction of the carbonic disulphide which has been studied by O. Loew.\* At least, it is certain that the monoclinic crystals contain a small amount of carbonaceous impurity, which they acquire from the solvent; and our theory is, that, under the action of the light, the crystalline molecules become as it were loaded by the adhesion of this material, and that the monoclinic habit is due to this circumstance. It may be mentioned, in this connection, that when the monoclinic crystals are redissolved in carbonic disulphide, and recrystallized, only a small part of the material, as a rule, retains the monoclinic form, the rest appearing in the more stable hexagonal condition. Still, there is a certain persistency of the new condition which would be natural with such a molecular adhesion as our theory assumes; and the remarkable adhesiveness of the material which is deposited by disulphide of carbon under the influence of the light is worthy of notice in this connection. Other facts bearing on this theory can be more intelligently discussed after this new form has been described.

The specific gravity of the monoclinic iodide of antimony was determined in the same way as that of the hexagonal modification (page 83), and with the following results:—

#### SPECIFIC GRAVITY OF MONOCLINIC ANTIMONIOUS IODIDE.

No.	Weight taken.	Sp. Gr. at 22°.
1.	1.2434	4.786
2.	2.2605	4.750
Mean value . . . . .		4.768

---

\* Am. Journal of Science (2), xlii. 363, and xli. 251.

It will be remembered that the mean value from five determinations of the specific gravity of the hexagonal modification was 4.848.

We made two analyses of the monoclinic iodide, each with a different preparation, and the iodine was determined as described in our previous paper. The small amount of impurity which would not dissolve in the tartaric acid solution was estimated in the first analysis, but not in the second, and we therefore give in each case the per cent of iodine in the crystals as they were weighed.

#### ANALYSES OF MONOCLINIC ANTIMONIOUS IODIDE.

No	Weight taken.	Weight of Ag. I obtained.	% of Iodine.
1.	1.3087	1.8332	75.73
2.	1.8988	2.6605	75.70
Mean value . . . . .			<u>75.715</u>
Theory when Sb=120 and I=127 . . .			<u>76.047</u>

The insoluble residue in the material of the first analysis weighed two and one-half milligrammes; and, were allowance made for this impurity, the corresponding percentage of iodine would be raised to 75.87. We found, however, that this material, like the hexagonal modification when crystallized from the same solvent, contained a trace of oxi-iodide of antimony, which of course must also be taken into the account before we can expect a close agreement with theory. So far as our analyses indicate, the total amount of impurity in the monoclinic crystals is not greater than that which we often find in the hexagonal crystals when crystallized, like the first, from a solution in carbonic disulphide. The difference seems to depend on the condition in which the impurity is present: and the conception we have formed is, that in the first case the impurity is a mere admixture like dirt entangled by the crystalline structure, while in the last case it actually adheres to the molecules. This molecular adhesion is induced by the action of the light; and our theory assumes, that, while the primitive molecules thus loaded are prevented from macling, so as to produce the triads of the hexagonal structure as shown in Fig. 1, so, also, these loaded molecules, when united in the normal way as shown in Fig. 2, form a crystal differing essentially, although still not very widely, from the now familiar orthorhombic prism of sixty and one hundred and twenty degrees.



The perfect isomerism of the monoclinic crystals with the other forms of antimonious iodide is shown by the readiness with which they change into the hexagonal iodide even more strikingly than by the above analyses. The general color of these crystals, like that of the orthorhombic crystals, is yellow; but the shade of color varies considerably under different circumstances, depending obviously on the impurity present. The purest crystals we have obtained had the same green tinge as the orthorhombic plates represented by Plate II., although less pronounced; and from this the tint varied through lemon yellow to quite dark brown, the brownish tinge evidently resulting from the free iodine, which, as we have said, frequently adheres to the crystals. Now, when heated, the monoclinic crystals (like the orthorhombic plates) acquire a red color and hexagonal structure at a temperature below that at which they melt. But the point of the change is by no means so definite as in the former case; and we observed circumstances connected with it obviously depending on the impurities present, which have an important bearing on the theory we have advanced above.

In the first place, we found that the yellow monoclinic crystals would bear a temperature of from  $120^{\circ}$  to  $125^{\circ}$ , without undergoing change. The experiments were conducted like those with the orthorhombic crystals already described (page 90); and comparative experiments were made in which the two modifications were heated side by side. The orthorhombic crystals were uniformly converted into the red modification at  $114^{\circ}$ , while the monoclinic were only slowly altered even at  $125^{\circ}$ . Of one experiment, we have the note, Some yellow crystals remain after heating for half an hour at  $125^{\circ}$ ; and of another, The change is gradual: the color deepens; the crystals become opaque, and soon after melt.

On the other hand, we observed that brownish crystals, which had been deposited from a solution containing a large excess of iodine, often reddened at the boiling point of water. In one experiment, in order to obtain a direct comparison, we heated for one hour side by side in a steam bath, portions of the following three different preparations:—

1. Greenish yellow orthorhombic plates obtained by sublimation.
2. Lemon yellow monoclinic crystals similar to the one figured on Plate I. Fig. 6.
3. Brownish monoclinic crystals evidently occluding free iodine.

Except the loss of evaporation, both 1 and 2 underwent no change, but 3 was wholly converted into the red modification. The change

was attended with some efflorescence, and the crystals generally became more or less opaque; but sometimes they retained their transparency quite perfectly, and we noticed instances in which the change spread through these crystals as through the orthorhombic plates before described. It is evidently the same change in both cases; and the best explanation we can give of the phenomena is, that, while the fixed carbonaceous occlusion, by loading the molecules, renders them less mobile, and thus tends to prevent the change, the volatile iodine, on the other hand, in breaking away from its attachment, destroys the unstable equilibrium of the molecules, and thus induces the change at a lower temperature than it would otherwise take place.

The habit of the clinorhombic or monoclinic crystals of antimonious iodide varies considerably under different conditions between prismatic and tabular forms. As in the case of the hexagonal iodide, the presence of an excess of iodine in the solution seems to determine the production of elongated prisms, while, after the solution has been freed from iodine, more tabular crystals are deposited. We measured numerous angles on crystals of these different types; and although the forms were obviously the same, and the similar angles very nearly equal, yet we observed differences in these angles amounting to fully half a degree, even when the several measurements must have been accurate to a minute. Such a variation in the angles was to be expected under the circumstances, and is wholly in harmony with the theory we have formed of the structure of these crystals. The crystal figured on Plate I. Fig. 6, and whose dimensions are given below, was selected from the product of the most successful crystallization we have yet made. On it were united all the forms we have observed on any of the crystals of this modification of antimonious iodide. It had a lemon yellow color, and was obviously of the tabular type. The crystal was very perfect, and most of the angles admitted of accurate measurement. The results are given below. They were verified by numerous repetitions of the measurements in zones and by comparison with similar angles measured on other crystals of the same preparation. As usual, we deduced the elements of the crystal from the measured values of three selected angles; and it will be noticed that the measurements of the other angles agree very closely with the values calculated from these data assumed to be fundamental. Indeed, we have seldom obtained better results with artificial crystals.

## CRYSTALLINE FORM OF ANTIMONIOUS IODIDE.

## MONOCLINIC VARIETY.

Forms {001}, {110}, {210}, {011}, {211}

Fig. 6, Plate I.

## FUNDAMENTAL ANGLES.

Between normals of 210 and 210 measured  $75^{\circ} 21'$ " " " 001 " 210 "  $105^{\circ} 30'$ " " " 001 " 211 "  $53^{\circ} 50'$ Angle of Axes  $70^{\circ} 16'$ Clinodiagonal,  $a = 1.6408$ Orthodiagonal,  $b = 1$ .Vertical,  $c = 0.6682$ 

	Measured.	Calculated.
Between normals of 100 and 210	$37^{\circ} 40\frac{1}{2}'$	$37^{\circ} 40\frac{1}{2}'$
" " " 210 " 110	$19^{\circ} 24'$	$19^{\circ} 24'$
" " " 110 " 110	$65^{\circ} 51'$	$65^{\circ} 51'$
" " " 001 " 110	$100^{\circ} 36'$	$100^{\circ} 34\frac{1}{2}'$
" " " 211 " 211	$61^{\circ} 37'$	$61^{\circ} 36'$
" " " 011 " 011		$115^{\circ} 40'$

Angle between basal edges made by {001} and {210}  $100^{\circ} 16'$ " " " " " " {001} " {110}  $62^{\circ} 44'$ Basal edge angle at end of clinodiagonal  $\left\{ \begin{array}{l} 100^{\circ} 16' \text{ corresponds to the} \\ \text{prismatic angle} \end{array} \right\} 104^{\circ} 39'$ Do.  $62^{\circ} 44'$  do.  $65^{\circ} 51'$ 

Vertical axis on the assumption that the forms {001}

and {211} are orthorhombic . . . . . 0.867

The crystals have a very well defined cleavage, parallel to the basal plane.

We endeavored to supplement the above crystallographic measurements by a study of the optical characters of the crystals; but, unfor-

tunately, in their natural state, these crystals were not well adapted to the purpose, and the best we have hitherto obtained have been too small, and the material too easily altered, to admit of the preparation of sections. We shall return to this work at the first opportunity, and we hope for better success in the future. For the present, we can only say that the axes of elasticity in the plane of symmetry make a small angle with the basal plane and its normal. With a minute and imperfect section, the rough measures which were alone possible under the microscope gave for the value of this angle about  $8^\circ$ . And, further, that we were unable to see the interference figure through the basal planes under conditions which were far more favorable than those under which the hyperbolas were seen through the orthorhombic plates: for the tabular monoclinic crystals we used in these observations were both larger and thicker than the plates; and, in order to secure an accurate comparison we examined the different crystals in succession. We also examined several cleavage sections parallel to the basal planes, with no better success; probably because the angle between the optical axes is sufficiently great to determine total reflection. The high index of refraction of the substance would naturally produce this effect at a very moderate value of the optical angle, and unfortunately the crystals at once lost their transparency when immersed in the liquids generally used in such cases.

The above results, although partial, are important as indicating a marked difference between the two classes of crystals we have last studied. Nevertheless, a comparison of measurements will show that the dimensions of the *basal section* of the monoclinic crystals differ by only two or three degrees from those of the orthorhombic plates before described. Thus, we have  $62^\circ 44'$  in place of  $60^\circ$ , and  $100^\circ 16'$  in place of  $98^\circ 13'$ ; and if, from the angle of the hemioctahedral plane on the basal section, we calculate the length of an assumed rectangular vertical axis, the value obtained (0.867) does not differ very greatly from the values of the corresponding axis for the chloride, bromide, and hexagonal iodide of antimony, as given on page 113. Moreover, on recrystallizing the monoclinic iodide from a solution in pure sulphide of carbon, we have in two instances obtained — mixed with the hexagonal iodide, which is always the chief product — microscopic rhombic plates showing all the planes of the octahedron, and whose angles (as nearly as they could be measured under the microscope) were  $60^\circ$  and  $120^\circ$ .

As it seems to us, the natural inference from the facts we have developed is the theory already intimated. According to this theory,

the monoclinic differs chemically from the orthorhombic iodide, only in containing a small amount of impurity. The molecules are supposed to be similarly constituted and similarly grouped together; but, by the adhesion of the impurity to the molecules, a certain difference of form results. This difference, although usually regarded as fundamental (for it is the difference between two crystalline systems), does not appear, as thus viewed, either great or essential; and the fact that similar differences of form are also met with in the mineral kingdom, among the micas, the vermiculites, and the chlorites, without the corresponding differences of chemical composition and physical qualities which an essentially different crystalline structure would imply, tends to sustain our theory. The subject is obviously one of great importance, and we may hope that the further study of these artificial products may serve to elucidate what has been a very obscure chapter in the science of mineralogy. We propose to continue the investigation, and as soon as larger and better crystals of the several conditions of antimonious iodide can be prepared, we shall repeat and complete the optical measurements. Meanwhile, we are studying the allied iodides, which promise further results. Every one who has had experience with this kind of work knows how easily an observer may fall into error by mistaking in these optical phenomena the delicate shades or features on which important distinctions frequently depend, and this is especially true when, as in the present case, the conditions are not the most favorable. An examination of larger and more perfect crystals will undoubtedly correct some of our data, and may modify some of our conclusions. The results here given are the best that could be obtained with the material at our command, and must be regarded as provisional until better material can be secured.

Tschermak maintains that the Muscovite micas are monoclinic crystals, of which the acute bisectrix makes a very small angle with the plane of cleavage; and it is possible that the crystals of antimonious chloride, bromide, and iodide, which we have studied, should partake of a similar structure; and that the thin, rhombic plates of antimonious iodide obtained by sublimation should differ from the monoclinic crystals of the same compound only in their habit. At least, with our present imperfect measurements, we cannot disprove such a theory; although the not necessarily incompatible theory advanced above seems to us the more probable of the two, and the only one which is consistent with the facts as they at present appear. Yet, if the other view should prove to be the more correct, the general result of the discussion in this paper would not be affected: only we must extend also

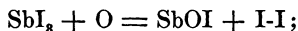
to such monoclinic crystals as we have described the principles here illustrated in regard to the relations of hexagonal forms.

The chlorites, the vermiculites, and the micas, whose crystallographic relations first suggested to us the theory of molecular macling, which the new facts developed in this paper have so fully confirmed, are all foliated minerals, of whose crystals the optical axis or acute bisectrix is either normal, or inclined at only a small angle to the plane of easy cleavage. With the crystals of antimonious iodide, both hexagonal and monoclinic, there is also an easy cleavage, parallel to the basal plane; and there is also a similar, if not an identical, relation of the optical axes. There is, however, no other evidence of a foliated structure, nor any sign of interlamination, such as we observed in those minerals. The crystals appear to be perfectly homogeneous, and (saving their great brittleness) cleave more like crystals of topaz than those of mica. The difference between the effect of interlamination and that which, as we suppose, results from molecular macling, must not be overlooked, although the optical phenomena in the two cases are so similar. What we called, in our paper on the vermiculites, interlaminar macling does not involve any essential change in the substance of the mineral; but molecular macling produces a new, although isomeric, substance. The red and the yellow antimonious iodides are as different substances as calcite and arragonite; and, as we conceive, the difference in the two cases is of the same kind.

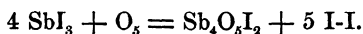
The facts developed in this paper all point to a more intimate relation between the different crystalline systems than has generally been supposed to exist, and are in complete harmony with the opinion we have frequently expressed, — that differences of crystalline system are not necessarily more fundamental than corresponding differences of dimension in the same system.

#### ANTIMONIOUS OXI-IODIDES ( $\text{SbOI}$ and $\text{Sb}_4\text{O}_5\text{I}_2$ ).

We have already, page 92, described the very remarkable chemical reaction which takes place when a solution of antimonious iodide in carbonic disulphide is exposed to the action of light and air. The reaction is chiefly that expressed by the formula, —



but this is, to a very limited extent, accompanied by the more complex reaction, —



The oxi-iodides of antimony, being insoluble in carbonic disulphide, are precipitated as an amorphous yellow powder, while the free iodine remaining in the solution changes its original greenish yellow color to a deep red, so deep that it soon appears black by reflected light. The change of color in the direct sunlight is very rapid, and forms a most striking phenomenon, which can readily be shown on the lecture table. When the direct rays of the sun are not available, the reaction can be produced by burning a few feet of magnesium ribbon. It is by far the most striking example of oxidation by the sun's light which has yet been discovered; and may, therefore, as a lecture experiment, be brought in striking contrast with the reduction of argentic chloride by the same agent,—a change which it rivals in extent, if not in rapidity. It has been maintained\* that while the more refrangible rays of the solar spectrum exert a reducing action on metallic compounds, both binaries and salts, the less refrangible rays (the yellow as well as the red) produce the contrary effect, and tend to increase the oxidizing action of the atmosphere. In the phenomenon we are studying, the oxidation is actually determined by the sun's light, and in the most marked manner; and, as this is the first definite example of such action which has been observed, it became a very interesting question to inquire, in what part of the solar spectrum the action was most intense. We therefore exposed the solution, in test-tubes, to the sun's rays at different parts of the solar spectrum, but under otherwise identical conditions; taking care, of course, to protect the tubes from any other radiation. The spectrum was projected in the usual way, with a lense and prism of glass; and we found that, while the brilliant red and yellow rays caused no sensible change of color, the comparatively faint blue and violet rays produced a very marked effect. Our method of experimenting was not delicate enough to show the precise point of maximum effect; but it was evident that the whole order of the phenomena was the same as in the case of argentic chloride and similar photographic preparations.

As we have before stated, the solution of iodide of antimony undergoes no change in contact with ordinary air, so long as it is kept in the dark; and since the amount of iodine set free under the influence of the light can be readily estimated, and since this is the measure of the chemical action, it is evident that the new reaction affords a direct

---

\* *Étude sur la Part de la Lumière dans les Actions Chimiques, et en particulier dans les Oxydations par M. P. Chastaing. Annales de Chimie et de Physique* (5), XI. 145. June, 1877.

means of measuring the amount of chemical change caused by solar radiation.

We have also stated, that, even in the dark, iodide of antimony is oxidized by ozone. The experiment is easily made by passing through the disulphide of carbon solution a current of air which has been ozonized by electricity. The action is very marked, but not so rapid as in the direct sunlight. The products are the same in both cases, — oxi-iodide of antimony and free iodine; and, under the influence of the sun's direct rays, all the iodide of antimony can be thus, with time, removed from the solution.

The reaction we are considering was first observed in a closed flask, and the circumstances were such that we did not at first suspect the important part which the atmospheric air played in the process. This however, became evident as soon as we had examined the products of the reaction; and we then made experiments to determine whether any reaction would take place out of contact with the air. For this purpose, we sealed up the solution in flasks from which the air had been displaced by carbonic dioxide, and, under these conditions, exposed the solution to the direct sun's light. But, although it was easy in this way to preclude any considerable change, we did not succeed in preventing it altogether. A slight reddening and turbidity indicated at least the beginning of oxidation, and this we traced to the oxygen gas held in solution by carbonic disulphide. But, after this small amount was exhausted, the action was wholly arrested, though we exposed the solution for days to the brightest sunlight.

Carbonic disulphide obviously aids the reaction by dissolving oxygen gas, as well as antimonious iodide; but we must not overlook what we stated in the previous paper, — that the same oxidation may take place independently of this solvent. The crystals of antimonious iodide, the yellow as well as the red, soon become coated with oxi-iodide, when exposed to the light and air; and we have lost a number of fine specimens from this cause. Under the microscope, the oxi-iodide appears as a yellow efflorescence, which soon destroys the transparency of the mass; and the odor of free iodine can be perceived on opening the bottle in which the preparation has been kept. This action, of course, is comparatively slow, but not less definite than that which we have been previously considering.

The oxi-iodide which, during oxidation, falls from the solution of antimonious iodide, is an amorphous yellow or brownish yellow powder. As it is insoluble in carbonic disulphide, it can easily be separated and cleaned by filtration and washing with this liquid. We made analyses of three different preparations, with the following results: —



## ANALYSES OF ANTIMONIOUS OXI-IODIDE.

No.	Weight taken.	Weight of AgI obtained.	% of Iodine.
1.	0.1105	0.0837	40.94
2.	0.5728	0.4511	42.56
3.	0.2411	0.2059	46.15
		Theory for SbOI	48.29
		„ „ Sb <sub>4</sub> O <sub>5</sub> I <sub>2</sub>	31.20

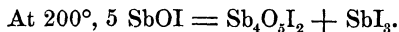
Whence it is evident that the material consists chiefly of SbOI; and, by regulating the action, this substance can be thus obtained in a nearly pure condition, as the last analysis shows.

The chemical constitution of the precipitated oxi-iodide is also very plainly indicated by the successive changes which it undergoes when heated in an atmosphere of inert gas, especially if they are studied in connection with the precisely similar changes which the well crystallized, and therefore more definite, oxichloride of antimony (SbOCl) undergoes under the same conditions as already described, page 63, of this volume. We experimented on the oxi-iodide with the apparatus also described and figured in our previous paper; and we found that, from the dried precipitate, when heated in a current of carbonic dioxide gas, antimonious iodide begins to sublime at 150°. At 200°, the sublimation became active, and continued until a definite amount of SbI<sub>3</sub> has been driven off, when it wholly ceased. In external appearance, the residue differed only slightly from the original substance; but when analyzed it gave the following result:—

Analysis of residue after heating at 200°, until sublimation ceased.

Weight taken.	Weight of AgI obtained.	% of Iodine.
1.8853	1.1512	32.99

On now heating the residue more intensely, it underwent no further change until the temperature rose above 350°; but, at a low red heat, antimonious iodide again sublimed, and there was left, as the final residue, beautifully crystallized antimonious oxide — both orthorhombic prisms and octahedrons. The reactions were obviously these:—



On examining the residue of the last reaction, before the change was complete, we have observed, mixed with the very brilliant colorless crystals of antimonious oxide, faintly yellow crystals, which had a well-marked monoclinic form, resembling that of the crystals of antimonious oxichloride ( $\text{Sb}_4\text{O}_5\text{Cl}_2$ ); which are deposited from aqueous solutions of antimonious chloride which contains a deficiency of tartaric acid, and which we shall describe hereafter. These crystals were only microscopic objects, and far too small both in size and quantity for chemical analysis or crystallographic measurement. We were, however, able to prove, both that they contained iodine, and that they were converted into  $\text{Sb}_2\text{O}_3$ , on further heating; and there can be, therefore, no question that they were crystallized,  $\text{Sb}_4\text{O}_5\text{I}_2$ .

#### ANTIMONIOUS OXIBROMIDES ( $\text{SbOBr}$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ ).

Under the influence of the air and the direct sunlight, a solution of antimonious bromide undergoes a slow oxidation like that we have just studied, but to a far less extent. Bromine is set free, and an oxibromide of antimony is deposited in an amorphous brownish powder; but the action is so slight, that, even after several weeks' exposure, we were unable to obtain, from a considerable volume of the solution, a sufficient amount of the precipitate for analysis. We were only able to prove that, like  $\text{SbOI}$ , it is decomposed when heated in two stages, leaving a residue of  $\text{Sb}_2\text{O}_3$ ; but this reaction was sufficient to indicate that it consisted mainly, at least, of  $\text{SbOBr}$ . The precipitate contained a considerable amount of carbonaceous material, also separated from the solvent by the light; and it evidently owed its color to this impurity. Pure  $\text{SbOBr}$  would undoubtedly be colorless.

The compound  $\text{Sb}_4\text{O}_5\text{Br}_2$  can readily be obtained, by heating in a sealed tube, to a temperature of  $160^\circ$ , a mixture of antimonious bromide and absolute alcohol, according to the method employed by Schaeffer\* for preparing the oxichlorides. Some beautifully crystalline oxibromide has been recently prepared in this way by Mr. Clifford Richardson, a student of this laboratory. The crystals were distinctly monoclinic, although too small for measurement. Mr. Richardson's analysis gave the following result:—

---

\* Berichte der Deutschen Chem. Gesell. 1868.

## ANALYSIS OF ANTIMONIOUS OXIBROMIDE.

## PREPARED WITH ALCOHOL.

Weight taken.	Weight of AgBr obtained.	% of Bromine.
0.6634	0.3424	21.96
Theory for $\text{Sb}_4\text{O}_5\text{Br}_2$ when $\text{Sb} = 120$		22.22

Several attempts were made to prepare  $\text{SbOBr}$ , by using a larger proportion of antimonious bromide as compared with the alcohol, according to the indications furnished by Schaeffer's experiments with antimonious chloride; but the product was uniformly  $\text{Sb}_4\text{O}_5\text{Br}_2$ ; nor have we been, as yet, more successful in isolating the compound in other ways.\* An analysis of the white amorphous precipitate formed by the action of water on antimonious bromide showed that it also consisted essentially of the same,  $\text{Sb}_4\text{O}_5\text{Br}_2$ . The following result was obtained by Mr. Richardson:—

## ANALYSIS OF ANTIMONIOUS OXIBROMIDE.

## PRECIPITATED BY WATER.

Weight taken.	Weight of AgBr obtained.	% of Bromide.
0.2281 gramme.	0.1155	21.54

ANTIMONIOUS OXICHLORIDES ( $\text{SbOCl}$  and  $\text{Sb}_4\text{O}_5\text{Cl}_2$ ).

These two compounds were prepared in a crystalline condition by following the directions given by Schaeffer in the paper already referred to. The crystals of  $\text{SbOCl}$  were not described by Schaeffer. Those obtained by Mr. Richardson were from half a millimetre to a millimetre in length, and enabled us to determine their crystallographic dimensions with approximate accuracy. They were evidently monoclinic, and presented the planes of an oblique rhombic prism with a klinodome and pinacoids.

---

\* We also tried to prepare crystallized oxi-iodides of antimony by Schaeffer's method, but without success. A solution of antimonious iodide in absolute alcohol yields, without heating, an abundant precipitate of oxi-iodide, but as a perfectly amorphous powder. The material was evidently a mixture of the two oxi-iodides we have distinguished. Analysis gave for one preparation 46%, and for another 40.58%, of iodine.

CRYSTALLINE FORM OF ANTIMONIOUS OXICHLORIDE ( $\text{SbOCl}$ ).

PREPARED BY SCHAEFFER'S METHOD.

MONOCLINIC SYSTEM.

Forms  $\{110\}$ ,  $\{011\}$ ,  $\{001\}$ 

Fig. 7, Plate I.

ANGLES MEASURED.

Between normals, —

110 on $\overline{1}10$	$98^{\circ} 2'$
011 „ 0 $\overline{1}1$	$107^{\circ} 14'$
110 „ 001	$100^{\circ} 8'$
001 „ $\overline{1}10$	$79^{\circ} 52'$

From these we calculated :—

Clinodiagonal,  $a = 0.8936$ Orthodiagonal,  $b = 1$ Vertical,  $c = 0.7587$ Angle of Axes,  $= 76^{\circ} 31'$ 

By referring to page 97, it will be seen that these crystals are closely isomorphous with those of the monoclinic, antimonious iodide. We examined them also with a polarizing microscope, and found that, when the light passed normally to the prismatic faces, the principal optical sections made angles of  $40^{\circ}$  and  $50^{\circ}$ , respectively, with the prismatic edges.

The following analyses were made by Mr. Richardson. In the first three, the oxichloride was decomposed by boiling over it a solution of pure sodic carbonate. In the last, it was dissolved in a concentrated aqueous solution of tartaric acid.

ANALYSES OF  $\text{SbOCl}$ .

PREPARED BY SCHAEFFER'S PROCESS.

No.	Weight taken.	Weight of AgCl obtained.	% of Chlorine.
1.	0.5055 gram.	0.4158 gram.	20.35
2.	0.7268 „	0.5997 „	20.41
3.	0.8367 „	0.6915 „	20.45
4.	0.5476 „	0.4488 „	20.28

Mean value . . . . . 20.37

Theory  $\text{Sb} = 120$  . . . . . 20.70

The want of closer agreement in the results, both with each other and with theory, we traced to a slight admixture of  $\text{Sb}_4\text{O}_5\text{Cl}_2$ ; and we found that this last compound was by far the more readily formed of the two, and, except in the single experiment by which the preparation subsequently analyzed was obtained, the chief product of the reaction was largely mixed with the more oxygenated compound, even when the prescribed formula had been closely followed.

By operating with several hundred grammes of antimonious chloride and alcohol, we obtained the compound  $\text{Sb}_4\text{O}_5\text{Cl}_2$  in beautiful large crystals, some of which were over a centimetre in length. We used for the purpose a cylindrical vessel of platinum, having a capacity of about 300 cubic centimetres; which, when covered with a lid of the same material, fitted exactly the interior of a Papin's digester, made nearly after the pattern recommended by Frankland.\* This device was suggested by the "soda-water" fountains described on page 118 of the previous volume of these "Proceedings." The outside shell of such fountains must necessarily be very strong, and is now often made of steel plates; but the aerated water is held by an interior vessel, which, though independent of the shell, forms its lining. This inner vessel may be even of glass, for it bears no strain; since a small aperture through the neck equalizes the pressure on the outer and inner surfaces, and the "lining" fits the shell so tightly that no space is left into which the contents can overflow.

The general form of the crystals of  $\text{Sb}_4\text{O}_5\text{Cl}_2$ , prepared as we have described, is shown by Fig. 8, Plate I., and they are evidently more highly modified than those figured by Schaeffer. They are frequently terminated at the two ends, and usually differently terminated, as our drawing represents. At one end, we have an acute tetrahedral solid angle, formed by the meeting of the planes of a hemioctahedron with those of a vertical dome, while at the other end we have an edge formed by the meeting of the single basal plane with the single plane of an orthodome found on the crystal. These crystals thus present a very striking example of hemihedrism at the terminations, and we propose to examine hereafter their polar relations. The faces have a high vitreous lustre, and many of the angles can be measured with great precision. Unfortunately, however, but as a natural result of the multiplication of the octahedral planes, the faces of the principal prism are generally striated parallel to the basal intersections, and this striation renders more or less uncertain the measurements of the angles

---

\* Watt's Dictionary of Chemistry, article *Bath*, i. 520.

between the octahedral and the prismatic faces, on which we had chiefly to depend for determining the position of the vertical axis. The value of the angle  $\overline{112}$  on  $\overline{110}$ , which we selected as one of the fundamental data, was obtained by comparing a number of crystals on which the condition of the faces was especially favorable, and is the most probable value deduced from many observations. Nevertheless, this is the one doubtful element, and may be in error to the extent of a few minutes. The result was checked by measuring the angle of  $\overline{112}$  on  $\overline{110}$ , which, although not favorably situated as a measure of the fundamental dimensions of the crystal, was useful as a proof of the accuracy of the work by which they were deduced; and the table below shows how well it bears this test. As in this last measurement, the reflected image of the signal crossed the striations at nearly  $90^\circ$ , the signal was comparatively well defined; and the same was true in the measurements of the prismatic angles, which agreed very closely on different crystals. The hemioctahedral planes  $\{\overline{112}\}$  were by far the best developed of all the planes of this class; but we selected in preference, as the fundamental octahedron, a subordinate form  $\{\overline{111}\}$ , to which the associated planes bore a simpler numerical relation. The planes  $\{\overline{113}\}$  were so small that the reflection of the signal was seen only by flashes. The planes  $\{\overline{331}\}$  were the best defined of an indefinite zone between  $\{\overline{111}\}$  and  $\{\overline{110}\}$ ; among which others, with still higher parameters, might have been doubtfully distinguished. We have previously called attention to similar zones of planes\* with high but yet definite numerical ratios. They are by no means an exceptional phenomenon, and their crystallographic interpretation seems to us worthy of more attention than it has received. The result of our measurement is given in the following table:—

# CRYSTALLINE FORM OF ANTIMONIOUS OXICHLORIDE ( $\text{Sb}_4\text{O}_5\text{Cl}_2$ ).

PREPARED BY SCHAEFFER'S METHOD.

MONOCLINIC SYSTEM.

Forms  $\{\overline{110}\}$ ,  $\{\overline{111}\}$ ,  $\{\overline{112}\}$ ,  $\{\overline{113}\}$ ,  $\{\overline{331}\}$ ,  $\sigma \{\overline{101}\}$ ,  $\sigma \{\overline{100}\}$

Fig. 8, Plate I.

## FUNDAMENTAL ANGLES.

Between planes	$\overline{110}$ and $\overline{110}$	$86^\circ 49'$
"	" $\overline{112}$ " $\overline{110}$	$156^\circ 42'$
"	" $\overline{112}$ " $\overline{112}$	$112^\circ 7'$

---

\* These Proceedings, vol. iii., page 87.

From these, we calculated —

Clinodiagonal,  $a = 1.239$

Orthodiagonal,  $b = 1$ .

Vertical Axis,  $c = 3.082$

Angle of Axes,  $C = 58^\circ 38'$

#### ANGLES ARRANGED IN SERIES.

			Calculated.	Observed.
Between normals	00I	and 11 $\bar{2}$	45° 45'	45° 47'
"	"	00I " 11I	55° 50'	55° 53'
"	"	00I " 33I	64° 17'	
"	"	00I " 110	69° 3'	68° 50'
"	"	00I " 10I	97° 54'	97° 33'
"	"	110 " 110	86° 49'	86° 49'
"	"	110 " 331	88° 47'	88° 38'
"	"	110 " 111	92° 12'	
"	"	110 " 112	96° 11'	96° 14'
"	"	110 " 113	99° 12'	99° 2'
"	"	113 " 113	57° 30'	
"	"	112 " 112	67° 53'	67° 53'
"	"	111 " 111	80° 9'	
"	"	331 " 331	89° 2'	
"	"	110 " 110	93° 11'	93° 11'
"	"	110 " 331	4° 46'	
"	"	110 " 111	13° 13'	
"	"	110 " 112	23° 18'	23° 18'
"	"	110 " 113	30° 52'	

We have not been able to study in detail the optical characters of these crystals; but observations with the polarizing microscope indicate, that, when resting on their prismatic planes, one of the principal optical sections is approximately, but not quite, parallel to the prismatic edges, making an angle with it of about  $5^\circ$ .

An analysis of the above crystals, made by Mr. Richardson, gave the following results: —

ANALYSIS OF ANTIMONIOUS OXICHLORIDE ( $\text{Sb}_4\text{O}_5\text{Cl}_2$ ).

PREPARED BY SCHAEFFER'S PROCESS.

Weight taken.	Weight of AgCl obtained.	% of Chlorine.
0.6376	0.2879	11.17
Theory for $\text{Sb}_4\text{O}_5\text{Cl}_2$ when $\text{Sb} = 120$		11.25

We have already stated that this same compound is deposited from aqueous solutions of antimonious chloride containing less than a definite proportion of tartaric acid, under conditions which are given at length in our previous paper (page 23, of this volume). The crystals thus obtained differ wholly in general aspect from those we have just described. While the former were acicular, these are tabular, and, instead of being isolated, generally group themselves in tufts; which, although sometimes a millimetre in diameter, consist of crystals so small and so closely compacted together, that hitherto we have found it impracticable to separate and measure them. As seen under the microscope, the crystals appear distinctly monoclinic; the tufts presenting terminations similar to those of epidote, and the crystals showing the same tendency to growth in the direction of the orthodiagonal which is so characteristic of that mineral species; while, at the same time, the packing together of the tabular crystals in tufts recalls the phenomenon so familiar on specimens of calamine and prehnite. Assuming that the terminal planes at the ends of the orthodiagonal are the planes of a vertical prism, and the plane of twining the basal plane, then such rough estimates of the axial inclination as we have been able to make with the microscope would indicate that these crystals are much less oblique than the last, and more closely allied in form to the crystals of  $\text{SbOCl}$  before described. Like these, they frequently present the planes of a klinodome  $\{011\}$ , Fig. 7, Plate I., which never appear on the other type of crystals (Fig. 8), and indeed would hardly be compatible with it. By regulating more carefully the amount of tartaric acid in the solution, we hope to obtain hereafter larger crystals of this last variety of  $\text{Sb}_4\text{O}_5\text{Cl}_2$ , whose exact measurement will settle the question in regard to the relation of the two forms.

We analyzed with great care the crystals of  $\text{Sb}_4\text{O}_5\text{Cl}_2$  deposited by the tartaric acid solution, in order to obtain additional evidence in regard to the atomic weight of antimony. By the methods already described, both the antimony and the chlorine were determined; while the oxygen was estimated, as is usual, by loss. The following are our results:—



ANALYSIS OF ANTIMONIOUS OXICHLORIDE ( $\text{Sb}_4\text{O}_5\text{Cl}_2$ ).

CRYSTALLIZED FROM A TARTARIC-ACID SOLUTION.

	Found.	Theory.
Antimony . .	76.10	76.06
Chlorine . .	11.22	11.25
Oxygen . .	12.68	12.68
	<hr/> 100.	<hr/> 100.

We also determined the specific gravity of these same crystals; which we found to be, at the ordinary temperature, 5.014.

OXICHLORIDE OF ANTIMONY ( $\text{Sb}_8\text{O}_{11}\text{Cl}_2$ ).

As is well known, precipitated oxichloride of antimony (powder of Algaroth), when washed with hot water, undergoes a gradual decomposition; yielding after long-continued washing pure antimonious oxide, and hydrochloric acid, which is removed by the water. It is also known that, if the snow-white bulky precipitate is left under the liquid for a few days, it forms a grayish white mass, consisting of brilliant microscopic crystals, which are described by Johnston and Miller as oblique, rectangular prisms, having the obtuse summits replaced by planes. The amorphous precipitate is undoubtedly a mixture of the two compounds we have just studied, in varying proportions, depending on the conditions of the precipitation; but the crystals are evidently  $\text{Sb}_4\text{O}_5\text{Cl}_2$ . Johnston's analysis gives the exact theoretical per cent of chlorine (11.25); and the mean of two analyses by Peligot gives the same.\* We can find no satisfactory evidence of a definite compound between  $\text{SbOCl}$  and  $\text{Sb}_4\text{O}_5\text{Cl}_2$ ; and the fact that, when gradually heated,  $\text{SbOCl}$  manifests but one stage in its decomposition, seems to indicate that such a compound cannot exist. We have carefully studied this decomposition, and we would refer to the description of the phenomena which we gave in our previous paper, page 63, of this volume.† There

---

\* Gmelin's Hand-book of Chemistry, Cavendish edition, iv. 367.

† The decomposition of the antimonious oxichlorides by heat, after the manner we have previously described, affords the finest crystals of  $\text{Sb}_2\text{O}_3$  we have ever seen. These crystals are in part brilliant octahedrons (Seuarmonite), but chiefly orthorhombic prisms (Valentinite). The last are frequently highly modified, and terminated at both ends; affording an opportunity for a more complete crystallographic investigation of this substance.

was more probability that a definite compound might be isolated between  $\text{Sb}_4\text{O}_5\text{Cl}_2$  and  $\text{Sb}_2\text{O}_3$ ; and there is some evidence that such a compound had been analyzed.\* With the hope of obtaining an intermediate product, we exposed to the direct sunlight during the summer months of 1876, a quantity of precipitated oxichloride of antimony, under a very large volume of water, which contained, besides the hydrochloric acid resulting from the decomposition of antimonious chloride, also a small quantity of tartaric acid. During this time there formed a considerable quantity of small acicular crystals, that were easily washed clean from the light amorphous precipitate with which they were mixed. The crystal appeared under the microscope perfectly homogeneous, and their surfaces had a brilliant vitreous lustre. They were rhombic prisms, having one of the two pairs of prismatic edges truncated by pinacoid planes. They presented, however, no distinctive terminations, sometimes tapering on the four prismatic planes to a point, and at other times on the pinacoids to an edge. They had the aspect of trimetric crystals, resembling some forms of Arragonite; and, as accurately as could be determined with the polarizing apparatus of a microscope, the principal optical sections were parallel to the prismatic edge, in whatever position the prisms might lie on the stage of the instrument. Nevertheless, these characters are not conclusive; and a delicate oblique striation which we observed on some of the prismatic planes led us to suspect that the crystals are really monoclinic. An analysis of the above crystals, made by Mr. Richardson, gave the following results:—

ANALYSIS OF ANTIMONIOUS OXICHLORIDE ( $\text{Sb}_8\text{O}_{11}\text{Cl}_2$  ?).

No.	Weight taken.	Weight of AgCl obtained.	% of Chlorine.
1.	0.3605	0.0852	5.84
2.	0.7353	0.1759	5.91

Mean value . . . . . 5.875

Theory for  $\text{Sb}_8\text{O}_{11}\text{Cl}_2$  . . . . . 5.88

It is therefore probable that we have here the intermediate compound sought; although it is important that these observations should

---

\* Gmelin's Hand-book of Chemistry, Cavendish edition, iv. 367.

be confirmed by further experiments. The assumed compound would be the second member of a possible series of oxichlorides, whose molecules each contain two atoms of chlorine, and of which the compound  $\text{Sb}_2\text{O}_2\text{Cl}_2$  is the first term. In like manner,  $\text{SbOCl}$  is the first term of a parallel series, each of whose molecules contain one atom of chlorine, thus : —

## OXICHLORIDES OF ANTIMONY.

$\text{SbOCl}$	$\text{Sb}_2\text{O}_2\text{Cl}_2$
$\text{Sb}_3\text{O}_4\text{Cl}$	$\text{Sb}_4\text{O}_5\text{Cl}_2$
$\text{Sb}_5\text{O}_7\text{Cl}$	$\text{Sb}_6\text{O}_8\text{Cl}_2$
$\text{Sb}_7\text{O}_{10}\text{Cl}$	$\text{Sb}_8\text{O}_{11}\text{Cl}_2$

This table suggests, not only that there is a possibility of forming other compounds of this class, but also that there may be among them several isomers. On the next page, we give a table which offers a general review of the crystallographic relations of the more important antimonious compounds.

Our object in this paper has been to put on record a very considerable number of new facts ; and if, in presenting them in their philosophical relations, we have laid open numerous deficiencies in our knowledge which must be supplied by future investigation, we have only made evident, in the case of antimony, what is equally true of our knowledge of the chemical relations of many other equally common elementary substances. Some of these deficiencies we hope to be able to supply ourselves in future papers.

We would again express our obligations to the same gentlemen named at the close of the previous paper, for the assistance they have rendered in this portion of the investigation also. We are especially indebted to Dr. Gooch, for his aid in the crystallographic measurements ; and to Mr. Oliver W. Huntington, for the drawings with which the paper is illustrated.

## COMPARISON OF CRYSTALLINE FORMS OF ANTIMONIOUS COMPOUNDS.

## ORTHORHOMBIC.

Valentinite . . . . .	$\text{Sb}_2\text{O}_3$
Stibnite . . . . .	$\text{Sb}_2\text{S}_3$
Stibiozincite . . . . .	$\text{Sb}_2\text{Zn}_3$
Dyscrasite . . . . .	$\text{SbAg}_3$
Antimonious Chloride . . . . .	$\text{SbCl}_3$
Antimonious Bromide . . . . .	$\text{SbBr}_3$
$\alpha$ Antimonious Iodide . . . . .	$\text{SbI}_3$

## HEXAGONAL.

$\beta$ Antimonious Iodide . . . . .	$\text{SbI}_3$
--------------------------------------	----------------

## MONOCLINIC.

Antimonious Oxisulphide . . . . .	$\text{Sb}_2\text{OS}_2$
Antimonious Oxichloride . . . . .	$\text{Sb}_4\text{O}_5\text{Cl}_2$
Antimonious Oxibromide . . . . .	$\text{Sb}_4\text{O}_5\text{Br}_2$
Antimonious Oxi-iodide . . . . .	$\text{Sb}_4\text{O}_5\text{I}_2$
Antimonious Oxichloride . . . . .	$\text{SbOCl}$
$\gamma$ Antimonious Iodide . . . . .	$\text{SbI}_3$

Plate I.

Fig. 1.

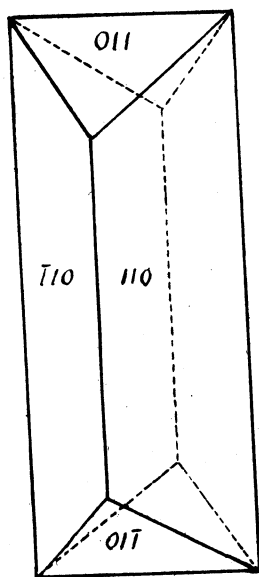


Fig. 2.

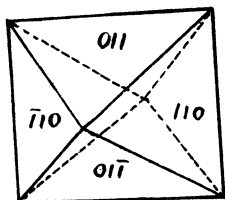


Fig. 8.

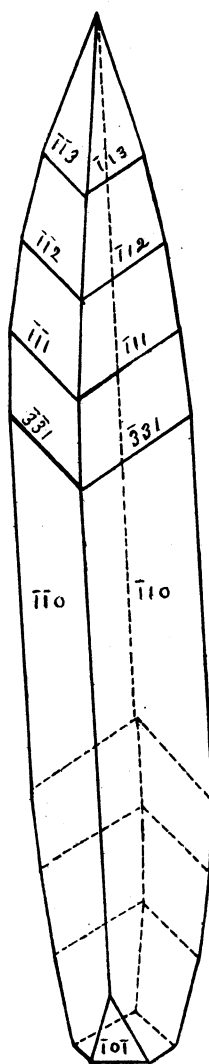


Fig. 7.

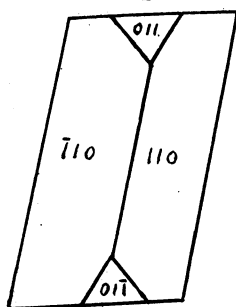


Fig. 3.

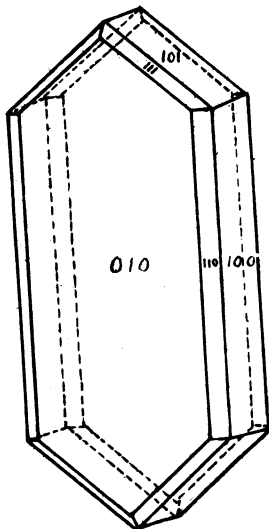


Fig. 5.

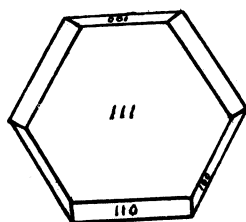


Fig. 6.

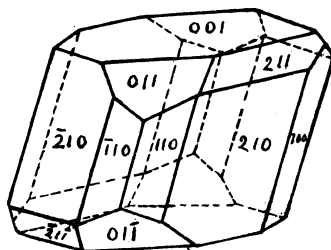


Fig. 4.

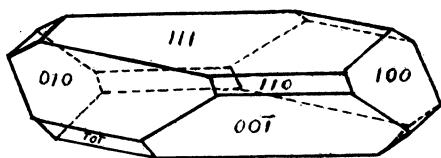


Plate II.

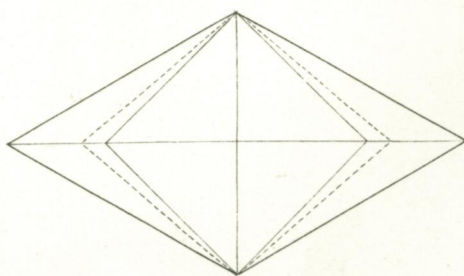
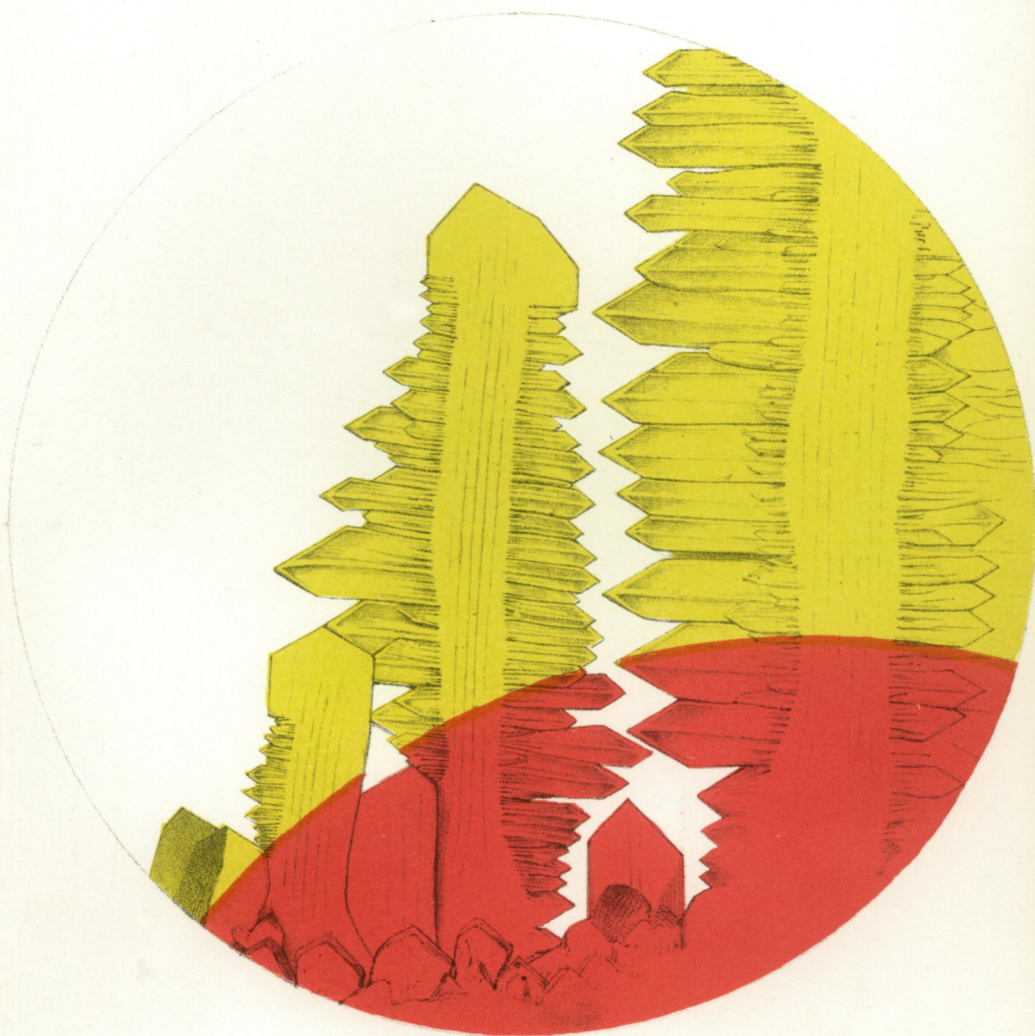


Plate III.

Fig. 1.

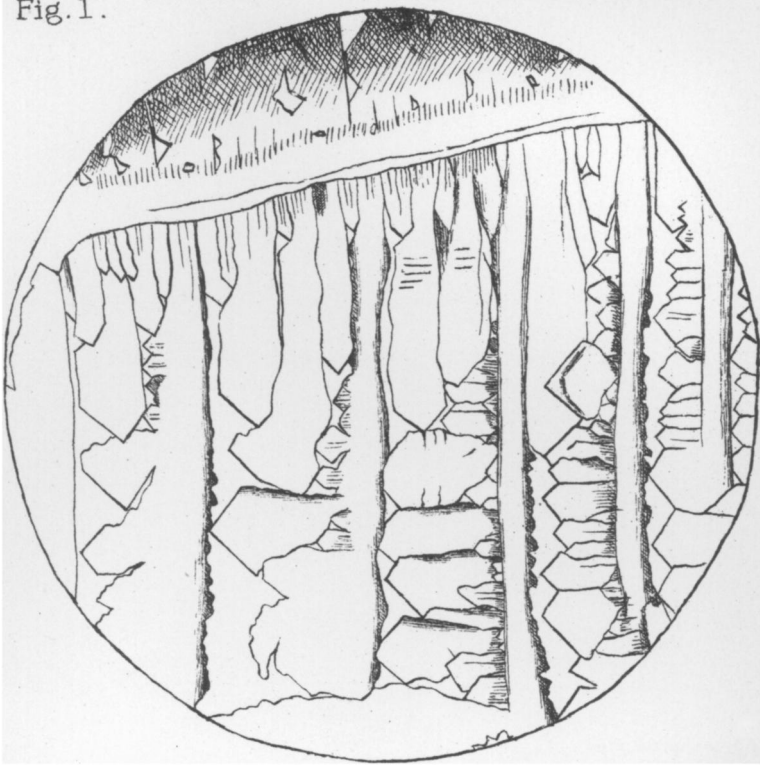


Fig. II.

